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RAPID PUBLICATION

Effect of Oxygen Partial Pressure on Structure and Dielectric Property of $BaTi_2O_5$ Films Prepared by Laser Ablation

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$BaTi_2O_5$ ferroelectric films were prepared on MgO (100) substrates by laser ablation at various oxygen partial pressures (P_{O2}). The effect of P_{O2} on the orientation, composition, surface morphology and dielectric property of the films was investigated. The molar ratio of Ti to Ba was independent of P_{O2}, almost in agreement with the stoichiometric composition of $BaTi_2O_5$. The $BaTi_2O_5$ films showed the orientation of (710) and (020) depending on P_{O2}. At $P_{O2} = 12.5$ Pa, (020) oriented $BaTi_2O_5$ film with an elongated granular and perpendicularly crossing texture was epitaxially grown on MgO (100) substrates. The $BaTi_2O_5$ film prepared at $P_{O2} = 12.5$ Pa exhibited a sharp permittivity maximum ($\varepsilon' \approx 2000$) at 750 K. [doi:10.2320/matertrans.48.625]

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Keywords: *$BaTi_2O_5$ films, laser ablation, structure, permittivity*

1. Introduction

Thin ferroelectric films with perovskite structure have attracted much attention due to the applications in high density dynamic random access memories (DRAM), non-volatile ferroelectric random access memories (FRAM) and optoelectronic devices.[1,2] In particular, $BaTiO_3$ (BTO), $PbTiO_3$ (PTO) and $PbZr_{1-x}Ti_xO_3$ (PZT) films have been extensively studied for their high dielectric constant and significant ferroelectricity.[3–7] However, these materials have drawbacks of too low Curie temperature for BTO ($T_c \approx$ 410 K) and environmentally unfriendly element (Pb) contained in PTO and PZT. Therefore, many researches have been conducted to develop a new lead-free material having a high T_c. Recently, a TiO_2-rich compound in the BaO-TiO_2 system, $BaTi_2O_5$, was found to be ferroelectric by our group[8,9] and Akishige *et al.*[10] Single crystalline $BaTi_2O_5$ prepared by floating zone and flux methods exhibited a significant permittivity peak at $T_c \approx 750$ K along the monoclinic b-direction. However, no research on $BaTi_2O_5$ films has been reported in spite of their potential applications as ferroelectric actuators and devices.

In order to obtain highly oriented ferroelectric $BaTi_2O_5$ films, the appropriate film deposition processing should be chosen to control the film structure and property. Many deposition techniques have been developed to obtain films, for example, sputtering,[11] metal-organic chemical vapor deposition (MOCVD),[12] sol-gel processing[13,14] and laser ablation.[15,16] The oxygen partial pressure can be a dominant deposition parameter, obviously affecting the oxygen deficiency, deposition rate and other characteristics of oxide films in those film processes. Since the laser ablation can be conducted in wide-ranged oxygen pressures, the preferred orientation of $BaTi_2O_5$ films may be controlled by adjusting oxygen partial pressure using laser ablation. It has been reported that the preferred orientation in the laser ablated $BaTiO_3$ films[3] changed from (001) to (100) with increasing oxygen partial pressure. In the present study, $BaTi_2O_5$ films were prepared by laser ablation, and the effect of oxygen partial pressure on the preferred orientation as well as composition, surface morphology and dielectric property was investigated.

2. Experimental

$BaTi_2O_5$ films were deposited on MgO (100) single crystal plate ($10 \times 10 \times$ H 0.5 mm) by laser ablation (TSLM-1000). A Q-switch pulsed Nd : YAG laser with a wavelength of 355 nm was used. The laser beam was introduced into a deposition chamber at an angle of 45° and focused on a rotating target. A hot-pressed $BaTi_2O_5$ pellet with a relative density of 96% was used as a target. MgO (100) substrate was placed parallel to the target at a distance of 50 mm. The chamber was evacuated to a high vacuum (1×10^{-6} Pa) and then the deposition was carried out under different oxygen partial pressures (P_{O2}) up to 20 Pa for 2 h. The substrate temperature (T_{sub}) was fixed at 973 K because $BaTi_2O_5$ phase was not obtained below 973 K. Table 1 summarizes the deposition parameters for preparing $BaTi_2O_5$ films.

The crystal structure was examined by X-ray diffraction ($\theta/2\theta$ scan) and pole figure (ϕ scan) with Cu Kα radiation (Rigaku, RAD-2C). The surface morphology was observed by a field emission scanning electron microscope (JEOL, SM-71010). The three-dimensional tapping mode AFM image over a scanning area of $2 \times 2\,\mu$m was taken by an atomic force microscope (TOYO, NANO SCOPE III) to measure the surface roughness. Electron probe X-ray micro-

Table 1 Deposition parameters for $BaTi_2O_5$ film prepared by laser ablation.

Deposition conditions	Parameters
Laser	Wave length: 355 nm Repetition rate: 10 Hz Pulse duration: 15 ns Energy density: 2×10^4 J/m^2
Target	$BaTi_2O_5$ pellet (ϕ 20 mm × H 3 mm)
Substrate	MgO (100) wafer (10 × 10 × H 0.5 mm)
Substrate temperature (T_{sub})	973 K
Oxygen partial pressure (P_{O2})	10^{-6}–20 Pa
Distance between target and substrate	50 mm

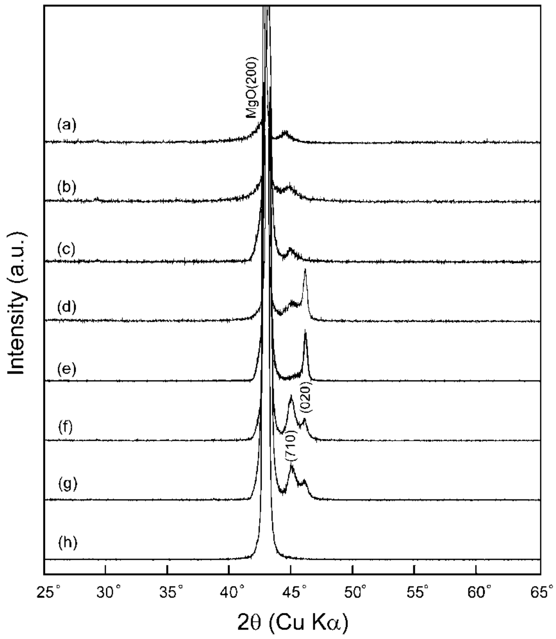

Fig. 1 XRD patterns of $BaTi_2O_5$ films prepared at $P_{O2} = 10^{-6}$ (a), 5 (b), 7.5 (c), 10 (d), 12.5 (e), 15 (f), 17.5 (g) and 20 Pa (h).

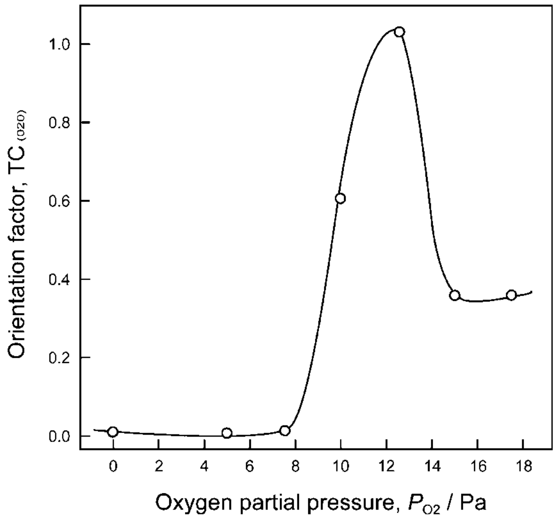

Fig. 2 Effect of oxygen partial pressure on orientation factor $TC_{(020)}$ of $BaTi_2O_5$ films.

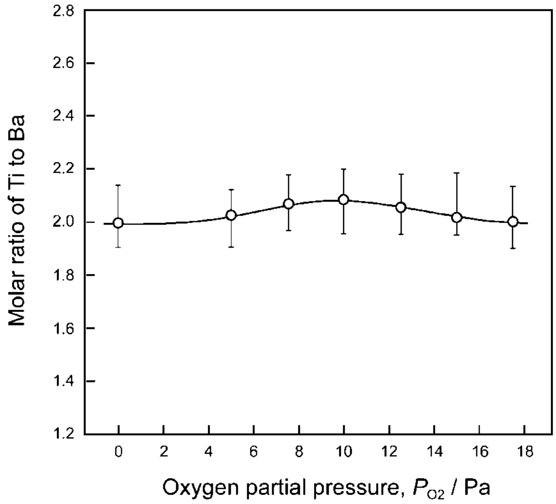

Fig. 3 Effect of oxygen partial pressure on molar ratio of Ti to Ba in $BaTi_2O_5$ films.

analyzer (JEOL, JXA-8621MX) was used to determine the composition, where seven spots were measured for each sample. The permittivity was measured by using an AC impedance analyzer (HP 4194) at a frequency of 100 kHz and in flowing Ar from room temperature to 973 K. DC sputtered Pt thin film (400 nm) and painted silver paste were used as bottom and top electrodes, respectively.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of $BaTi_2O_5$ films deposited at $P_{O2} = 10^{-6}$ to 20 Pa. Below $P_{O2} = 20$ Pa, the peaks from $BaTi_2O_5$ were identified, showing a (710) or (020) orientation. The $BaTi_2O_5$ films prepared at $P_{O2} = 10^{-6}$–7.5 Pa had a single peak indexed to (710). The full widths at half maximum (FWHM) of the (710) peak for $P_{O2} = 10^{-6}$ and 7.5 Pa were 1.23° and 1.14°, respectively. At $P_{O2} \geq 10$ Pa, the preferred orientation of $BaTi_2O_5$ was (710) and/or (020), depending on the P_{O2}. No $BaTi_2O_5$ phase was identified at $P_{O2} = 20$ Pa.

The preferred orientation of the $BaTi_2O_5$ films was evaluated by using an orientation factor $TC_{(020)}$ given by eq. (1).

$$TC_{(020)} = I_{(020)}/[I_{(020)} + I_{(710)}] \quad (1)$$

where, $I_{(020)}$ and $I_{(710)}$ are the intensities of (020) and (710) peaks of $BaTi_2O_5$, respectively.

Figure 2 depicts the relationship between P_{O2} and $TC_{(020)}$ of the $BaTi_2O_5$ films. $TC_{(020)}$ showed the highest value of 1.0 at $P_{O2} = 12.5$ Pa, implying that the film was completely oriented to (020). For $BaTi_2O_5$ crystals, the (020) plane should be one of the most stable planes.[8,9] The (710) plane is slanted from the (020) plane and would have higher energy than the (020) plane. At a too low P_{O2} ($P_{O2} < 10$ Pa), the ablated species would have excess kinetic energy on the substrate surface, forming a less stable plane, *i.e.*, (710) plane. On the other hand, at a too high P_{O2}, the ablated species would not have enough mobility to settle down at the stable plane[17,18] because they would lose the kinetic energy due to much collision in a gas phase. As a result, the films showed the (710) preferred orientation at $P_{O2} = 15$ and 17.5 Pa; furthermore, no $BaTi_2O_5$ crystal phase can be obtained at $P_{O2} = 20$ Pa. In the present study, the appropriate P_{O2} to form the stable (020) plane could be 10 to 12.5 Pa.

Figure 3 shows the effect of P_{O2} on molar ratio of Ti to Ba in the $BaTi_2O_5$ films. The ratios were around 2.0 to 2.1, almost in agreement with the stoichiometric composition of $BaTi_2O_5$.

Figure 4 shows the effect of P_{O2} on the surface morphology of the $BaTi_2O_5$ films. At $P_{O2} = 5$ Pa, small $BaTi_2O_5$ grains in a spherical shape were observed (Fig. 4(a)). The higher the P_{O2}, the more numbers the grains. At higher P_{O2}, the $BaTi_2O_5$ grains were elongated. At $P_{O2} = 12.5$ Pa, (020) oriented $BaTi_2O_5$ films with dense and elongated texture were obtained (Fig. 4(c)). Each grain was about 100 nm in length and 50 nm in width, and crossed rectangularly. At

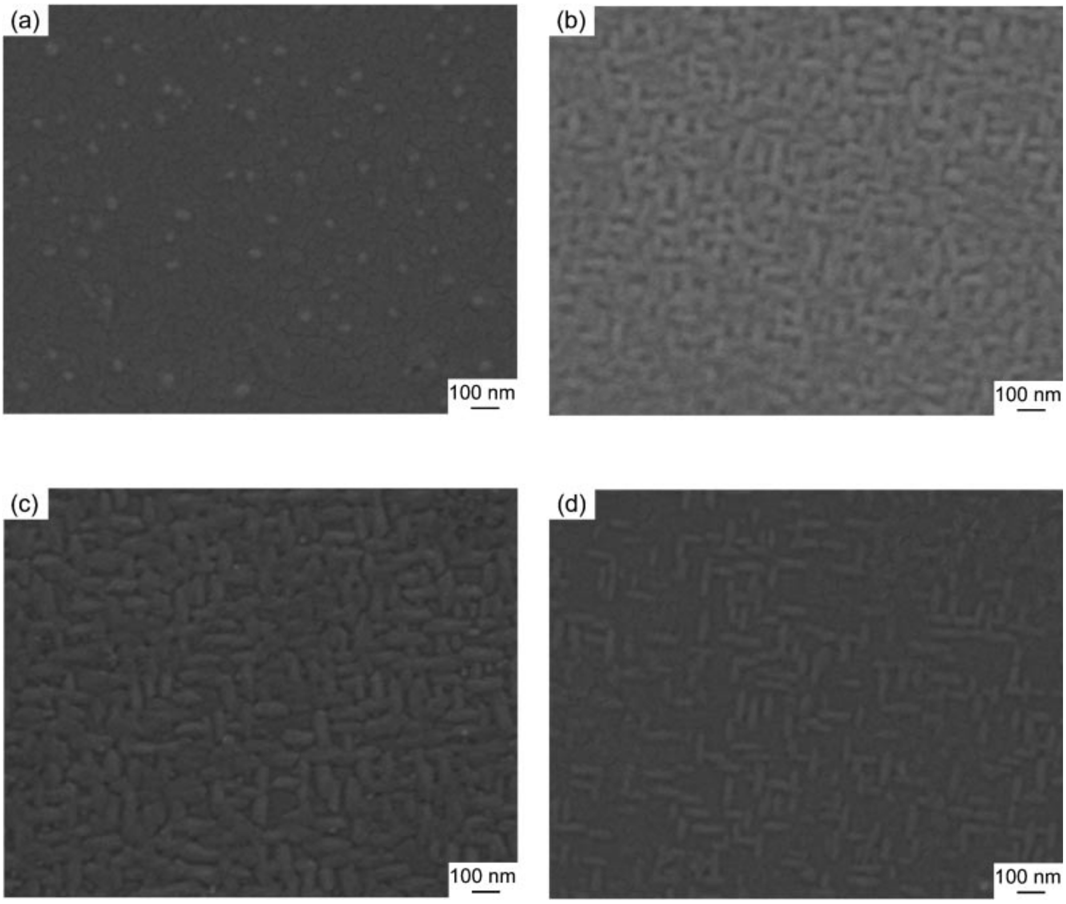

Fig. 4 SEM surface images of $BaTi_2O_5$ films prepared at $P_{O2} = 5$ (a), 10 (b), 12.5 (c), 15 Pa (d).

$P_{O2} = 15$ Pa, the texture of the elongated grains was disordered, where the (710) peak became the main peak (Fig. 1(f)).

Figure 5 demonstrates the X-ray pole figure of the (020) oriented $BaTi_2O_5$ film prepared at $P_{O2} = 12.5$ Pa, where the ϕ of $BaTi_2O_5$ (022) was scanned. Four diffraction spots were identified at $\alpha = 23°$, which was in agreement with the angle between $BaTi_2O_5$ (020) and (022). Since $BaTi_2O_5$ (022) is a two-fold symmetry, the four poles could indicate the two sets of two poles from $BaTi_2O_5$ (022) and $(02\bar{2})$ rotating 90°. The (020) oriented $BaTi_2O_5$ film had the rectangularly crossed texture (Fig. 4(c)), which could cause the four poles as schematically illustrated in Fig. 6. It is generally known that the lattice mismatch should be less than 1% for epitaxil growth. Since the a-axis length of $BaTi_2O_5$ is 0.39% greater than that of MgO, $BaTi_2O_5$ (020) can be epitaxially grown on MgO (100) substrate.

The effect of P_{O2} on the surface roughness (root mean square roughness, RMS) of $BaTi_2O_5$ films is illustrated in Fig. 7. The RMS increased from 3.2 to 6.7 nm with increasing P_{O2} from 5 to 15 Pa. At lower P_{O2}, the ablated species can arrive at substrate with a high kinetic energy due to less collision with ambient species.[3,19] This would lead to the high mobility of atoms and thus smooth surface at low P_{O2}.

Figure 8 shows the effect of temperature on the permittivity of $BaTi_2O_5$ films prepared at $P_{O2} = 5$ and 12.5 Pa having a weak (710) and a strong (020) orientation, respectively. The (710) oriented $BaTi_2O_5$ film prepared at $P_{O2} = 5$ Pa exhibited small permittivity from room temperature to 973 K, because the ferroelectricity of $BaTi_2O_5$ can be only observed in the b-direction. On the contrary, the (020) oriented $BaTi_2O_5$ film obtained at $P_{O2} = 12.5$ Pa had a significant peak of permittivity ($\varepsilon' \approx 2000$) at the Curie temperature (T_c) of $BaTi_2O_5$ (~ 750 K).[8]

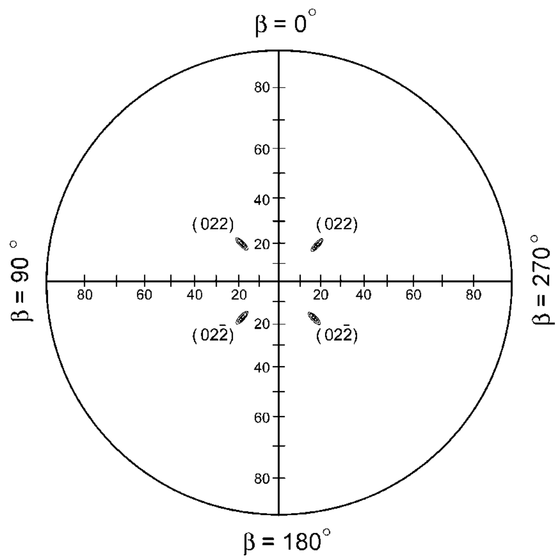

Fig. 5 X-ray pole figure of $BaTi_2O_5$ film prepared at $P_{O2} = 12.5$ Pa.

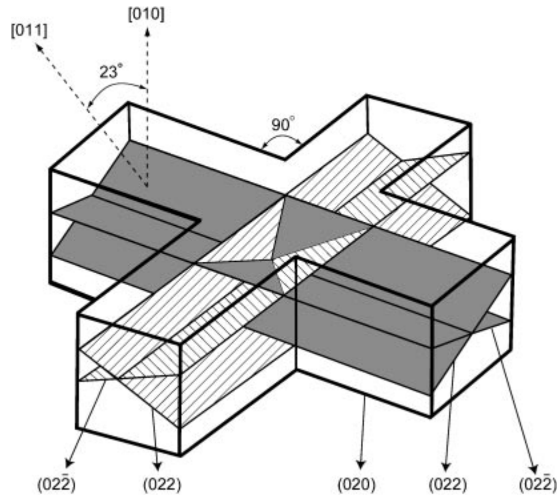

Fig. 6 Schematic configuration of $BaTi_2O_5$ crystal planes.

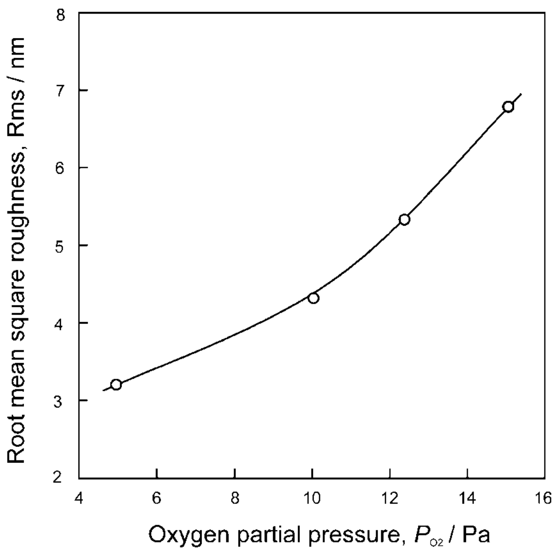

Fig. 7 Root mean square roughness of $BaTi_2O_5$ films as a function of P_{O2}.

4. Summary

$BaTi_2O_5$ films were prepared on MgO (100) substrates by laser ablation at various oxygen partial pressures (P_{O2}). The orientation of $BaTi_2O_5$ films changed from (710) to (020) depending on P_{O2}. The surface roughness increased with increasing P_{O2}. The molar ratio of Ti to Ba was almost 2.0 independent of P_{O2}. The optimum P_{O2} to obtain ferroelectric $BaTi_2O_5$ film was 12.5 Pa at $T_{sub} = 973$ K. The (020) oriented $BaTi_2O_5$ film with a dense and elongated texture was epitaxially grown on MgO (100) substrates. The $BaTi_2O_5$ film prepared at $P_{O2} = 12.5$ Pa exhibited a sharp permittivity maximum ($\varepsilon' \approx 2000$) at 750 K.

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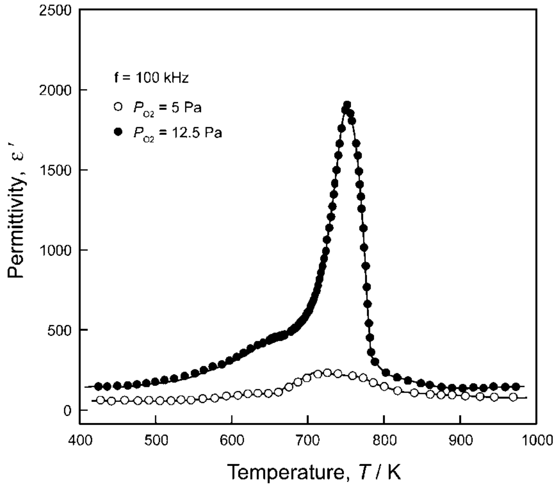

Fig. 8 Effect of temperature on the permittivity of $BaTi_2O_5$ films prepared at $P_{O2} = 5$ and 12.5 Pa.

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